

VACUUM EVAPORATION OF NATURAL AND SYNTHETIC HIBONITE SAMPLES.

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Introduction. According to equilibrium condensation calculations, corundum and hibonite are the earliest condensates from a cooling gas of solar composition [1]. Hibonite is a common minor mineral in many CAIs and, in recent years, a number of studies have focused on inclusions that consist predominantly of hibonite [2-7]. Trace element and isotopic compositions of these hibonite-bearing inclusions indicate a variety of formational processes, including condensation, distillation and crystallization from a melt; often multi-stage processes are required. Corundum-bearing inclusions are much rarer. Corundum occurs as a minor or trace phase in several CAIs [e.g., 8 and references therein] and a number of corundum grains have been isolated from Murchison and analyzed by ion microprobe [9]. In addition, this mineral occurs as a major phase, together with hibonite and minor perovskite, in two Murchison CAIs, BB-5 [10] and GR-1 [11].

We recently completed evaporation experiments on the Allende meteorite [12], in which we produced several hibonite-bearing residues that share many chemical and isotopic characteristics with the HAL-type hibonite inclusions for which an origin as distillation residues has been proposed [7]; we were able to show that many of the unique features of these inclusions can be produced in a single evaporation event. However, we did not observe corundum in any of our Allende evaporation residues. In this study we have, therefore, extended our experiments to the evaporation of hibonite itself in order to better understand the role of hibonite and its relationship to corundum in refractory inclusions. In addition, we evaporated two samples containing only synthetic oxides of the REE and other refractory trace elements (RTE) in order to examine the relative volatilities of these elements under vacuum evaporation conditions. Volatility-related fractionations of the REE are common in CAIs, but, with the exception of Ce and Eu depletions, appear to be difficult to recreate in laboratory experiments.

Experimental: Experiments were carried out on both natural and synthetically prepared hibonite. Fragments selected from a single crystal of Madagascar hibonite were evaporated at either 2100 °C or 2500 °C; this hibonite contains small amounts of Si, Mg and Fe, about 6 wt.% TiO₂ and 2 wt.% REE and is enriched in Th and U. Synthetic hibonite was prepared using high purity Al₂O₃ and CaCO₃ and doped with 0.8 wt.% MgO, 1.6 wt.% TiO₂ and approximately 200 ppm each

of the RTE Hf, Zr, Y, Sc, Nb, V, Sr and Ba and all 14 REE; these samples were evaporated at 2100 °C. Two samples containing subequal amounts of only the REE and RTE were evaporated at 2400 °C. All samples were heated at 100 °C/min. to their peak temperatures and held there for times between 1 and 120 minutes.

Results: Natural hibonite evaporation residues typically consist of corundum grains set in a glass matrix. In addition, these samples contain variable amounts of small grains of thorianite and a Ca-aluminate that is highly enriched in the REE (hereafter referred to as the ree-phase). Petrographic textures depend on evaporation temperatures: in residues evaporated at 2100 °C corundum grains are subhedral to euhedral and grow in size and abundance, relative to the glass matrix, with increasing mass loss. At high mass losses, the corundum crystals are often separated only by thin stringers of thorianite and the ree-phase. In contrast, hibonite residues evaporated at 2500 °C exhibit textures indicative of a reaction relationship between corundum and glass. The glass is typically present as elongated lathes and corundum occurs within and interstitial to it; these grains are small and show clear evidence of resorption into the glass. The proportion of corundum decreases with increasing mass loss and it is completely absent from the most refractory residue, which has a mass loss of 99.5 %. Synthetic hibonite residues were evaporated at 2100 °C and show textures similar to those of natural hibonite residues evaporated at the same temperature. These samples also contain tiny refractory-element-rich grains and one with a low mass loss contains small perovskite grains.

All Madagascar hibonite residues have MgO, FeO, SiO₂ and TiO₂ concentrations below EMP detection limits. Both the bulk compositions as well as individual phases (glass and the ree-phase) show decreasing Ca and Al concentrations and increasing REE and Th concentrations with increasing mass loss. Synthetic hibonite residues show similar compositional trends. Most refractory trace elements, including the REE, are uniformly enriched by up to a factor of 100 in the residues, relative to the starting material. However, Ce, V, U and, in the more refractory residues, Eu show volatility-related depletions that result from the dynamics of the evaporation process. We observed similar depletions in our Allende evaporation residues [12]. Ca isotopic compositions were measured in the natural hibonite residues and show enrichments in the heavy isotopes of up to 72 ‰/amu, consistent with a

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Rayleigh distillation process.

The two synthetic RTE residues, which experienced mass losses of 68 and 71 %, consist solely of homogeneous refractory element glass. Both samples have very similar RTE and REE patterns that are dominated by large depletions of V, Sr, Ba, Ce, Eu and Yb (Fig. 1); the Eu anomaly is larger than the Ce anomaly and Yb was below detection in most of the analyses. In addition, the LREE are depleted relative to the HREE, and La and Pr have somewhat lower abundances than Nd and Sm.

Discussion. Evaporation of hibonite produces corundum-bearing residues, as expected from phase equilibria considerations [13]. Thus, in principle, corundum-bearing inclusions, such as BB-5 and GR-1, may have a distillation origin. Hibonite from both BB-5 and GR-1 has lower Mg and Ti contents than most meteoritic hibonites and is, in this respect, similar to hibonite produced by evaporation of Allende [12]; in the present experiments glass from low mass loss residues is compositionally similar to these hibonites. However, both inclusions have isotopically light Mg and Ca [2], inconsistent with an origin through evaporation, although petrographic evidence suggests that GR-1 may have formed by partial melting accompanied by evaporation [11]. More promising candidates as evaporation residues may be the Group 2 corundum grains of [9]; these have low Ti and V, and mass fractionated oxygen isotopic compositions. The scarcity of corundum-bearing inclusions, however, suggests that melting of hibonite, with or without concomitant evaporation, was a rare process in the solar nebula.

Ultrarefractory REE patterns can originate either as early condensates from a cooling solar gas or as products of extreme evaporation of a material with initially chondritic REE abundances [14]. However, laboratory evaporation experiments have not been able

to recreate these patterns; large Yb depletions, such as those commonly observed in Group III inclusions are also difficult to reproduce. Through evaporation of a refractory-element-doped synthetic perovskite, Davis and Hashimoto [15] produced a REE pattern with a small Yb depletion and some offset of the LREE from the HREE; however no fractionations among the HREE were observed. These authors suggested that volatility-related fractionations of the REE are thermodynamically rather than kinetically controlled. By evaporating a mixture consisting solely of the RTE and REE oxides, we have carried out an extreme test of the effects of vacuum evaporation on the volatility-related fractionations observed in REE patterns. Although we observe a strong Yb depletion and depletion of the LREE relative to the HREE, there is no evidence of any fractionations among the HREE such as those that are found in ultrarefractory inclusions [14]. Thus, our results confirm the conclusions of [15]. Similarly, the extreme evaporation conditions required to generate Yb depletions suggests that most Group III REE patterns probably have a condensation origin.

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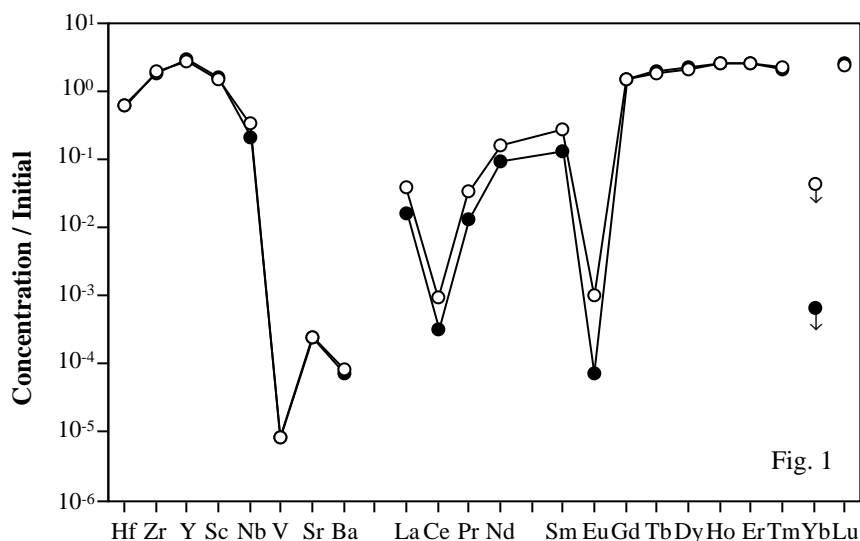


Fig. 1